THEORY OF THE IGNITION ENERGY OF CONDENSED EXPLOSIVES

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Introduction

The one-dimensional ignition of an explosive from a pure thermal heat source is known from experiment to require a certain critical energy per unit area from the initiating source, below which ignition will not occur even though the explosive adjacent to the source may be induced to undergo some chemical reaction. Thus, a self-sustained combustion (i.e., ignition) can result only when the rate of heat production by the chemical reaction of a certain requisite quantity of the explosive is greater than the rate of heat loss to the surroundings. As to whether the ignition results in normal combustion, or a thermal explosion followed by detonation is a matter which is related to the kinetic nature of the decomposition of the explosive, the heat flux from the initiating source, and the physical conditions (e.g., packing density, charge diameter, etc.) of the explosive. This topic is generally beyond the scope of this paper.

Experimental values of the thermal energy required to ignite an explosive are very meagre. Morgan [1] investigated the ignition of highly flammable solids by means of short hot wires and found a linear relationship between the critical ignition energy and the initiating time. Jones [2] confirmed this finding using a variety of match-head compositions. Bryan and Noonan [3] determined the minimum energies delivered in a 3 millisec interval that were just sufficient to ignite a unit area of several explosives and found values which ranged from greater than 0.4 cal/cm^2 for TNT, to less than 0.1 cal/cm^2 for lead styphnate.

The theory of ignition of solid combustibles has received detailed treatment [4], although the results are not generally discussed directly in terms of the ignition energy. This paper discusses the thermal ignition energies of explosives from the viewpoint of the heat conduction and kinetic processes involved.

Ignition Energy

When a step function heat source is brought in contact with a unit area of an explosive, heat flows into the explosive raising its temperature. An essentially constant temperature T_s is

established at the interface between the heat source and the explosive in a time very short compared to the ignition delay time of the explosive; its magnitude depends on several factors, including the temperature and energy content of the heat source, the intimacy of contact between the source and the explosive, and certain physical and chemical properties of the explosive. The temperature T at a given distance x within the explosive is given as a function of time t by (5):

$$T = T_o + (T_s - T_o) \, \text{erfc} \left[x/2(k_d t)^{\frac{1}{2}} \right] \tag{1}$$

where T_o is the initial temperature of the explosive, and k_d is its thermal diffusivity ($K/\rho C_p$), where K, ρ, C_p are the average coefficient of thermal conductivity, the density, and the average heat capacity, respectively. Chemical reaction is induced in the explosive at a rate consistent with the thermal decomposition kinetics and the local temperature of the explosive. For sufficiently low heat flux, ignition never occurs since heat conduction to the environment holds the temperature of the explosive low enough that self-heating does not occur. For higher heat flux, self-heating of the explosive does occur, and the time to explosion, which is calculable by the Frank-Kamanetski equation, depends on the size of the explosive. For sufficiently high heat flux, which is the case we consider in this paper, chemical reaction is initiated very rapidly due to the high surface temperature of the explosive. Self-sustained ignition occurs when the total conductive heat transfer from the source is sufficent to initiate a flame which will propagate with a velocity consistent with the ambient conditions for a requisite length that is determined by the thermal diffusivity and the burning velocity of the explosive. Under these conditions the reaction zone can further sustain itself from the explosive. For time periods less than that required to transfer the requisite energy, ignition will not occur even though local chemical reaction of the explosive takes place adjacent to the heat source. For time periods greater than that required to transfer the heat necessary to ignite the explosive the ignition energy becomes a function of the heating time.

The heat flux F through the surface of the explosive is obtained by multiplying the time derivative of Eq.(1), evaluated at $x = o$, by K. Substituting $E/t = F$ in the resulting expression gives:

$$E = (T_s - T_o)(K \rho C_p / \pi)^{\frac{1}{2}} t^{\frac{1}{2}} \tag{2}$$

where E is the energy per unit area conducted into the explosive.

There are various criteria for defining ignition. The usually considered criteria for ignition are defined by the conditions necessary for a transition from a pseudo-steady heat transfer to a non-steady process of reaction (4). For the present case we may consider this to occur when the heat

flux in the surface of the explosive due to chemical reaction is equal to 1/e that due to heat transfer from the source, since under this condition thermal initiation is underway adiabatically and the heat source can have very little further influence on the ignition process. However, the computations are relatively insensitive to the factor used in relating the chemical heat flux to that from the heat source. The heat flux due to chemical reaction is ρqv, where q is the heat of chemical reaction and v is the linear burning velocity consistent with the surface temperature. Quite generally,

$$v = LZexp(-E/RT_s) \qquad (3)$$

$L = (M/\rho N)^{1/3}$ is the monolayer thickness of the explosive, where M is the molecular weight, and N is Avogadro's number; Z and E are the Arrhenius kinetic parameters for the rate controlling thermal surface decomposition reaction of the explosive, and R is the gas constant. Hence for ignition:

$$(T_s - T_o)(K\rho C_p/\pi e^2 t)^{\frac{1}{2}} = \rho qLZexp(-E/RT_s) \qquad (4)$$

The ignition energies calculated by Eqs. (2) and (4) of several secondary explosives which were studied experimentally by Bryan and Noonan (3) for a 3 millisec heating period are summarized in Table 1. The computed values of T_s are also given. Values of K and C_p of $5(10^{-4})$ cal/(cm-sec $^{\circ}$K) and 0.44 cal/gm-$^{\circ}$K were employed; q was calculated assuming the oxygen in the explosive to first form CO, then H_2O, and finally CO_2. Values of 630, 814, 1220, and 1400 cal/gm were obtained for TNT, tetryl, RDX, and PETN, respectively. Crystalline densities were used, and the computations were performed using the available published decomposition kinetics.

Table 1. Comparison of Experimental and Theoretical Ignition Energies.

Explosive	Exptl E (cal/cm²)	E'	Computed T_s(°K)	E, Eqs. (2), (4). E	T_s
TNT	>0.38	0.75	1571	0.66[2]	1426
Tetryl	0.33	0.48	1098	0.34[3]	861
RDX	0.33	—	—	0.39[4]	935
PETN	0.25	0.34	858	0.25[5]	705
		0.21	638		

Kinetics from ref. 6; [2]ref. (7a); [3]ref. (7b); [4]ref. (7c); [5]ref.(7d).

The general agreement of the computed energies with the experimental values is very good; the perfect agreement in some cases is of course fortuitous since the estimated values of some of the parameters may be in error, and in any event the exact validity of the experimental data is not known. The factor 1/e

which was used to relate the conduction and reaction flux changes
(decreases) the computed energies by only about 10% from that of
using a factor of unity. However, the factor 1/e is believed
essentially correct since it roughly defines the inflection point
on an adiabatic rise in reaction rate.

Three things may be especially noted from Eqs. (2) and (4). The
ignition energy is a strong function of the temperature difference,
(T_s-T_0). Hence a high initial ambient temperature will lower the
energy required for ignition. This was previously noted by Hicks
(4b) on ignition delay time. The value of T_s is very sensitive
to the thermal decomposition kinetics for a fixed heating time;
the faster the decomposition rate (at a given temperature) the
lower the value of T_s. Thus initiating explosives usually re-
quire smaller initiating energies than do secondary explosives.
Finally it is seen that the ignition energy varies as the square
root of the heating time (for one-dimensional heating). This
was also noted by Hicks, and has been discussed in detail by
Yang (8). Yang also treated the line and point source cases,
and showed that the ignition energy varies as t and $t^{3/2}$
respectively in these cases. These results are directly trans-
posable to the present treatment. The influence of the heating
time on the ignition energy given in Eq. (2), in Hick's paper,
and in the paper of Yang is consistent with the experimental
observations of Jones (2) on solid explosives, and Jones and
Stout (9) on gaseous explosives.

The ignition time t_i for a fixed T_s is given by
Eq. (4):

$$t_i = a(T_s-T_0)^2 \exp(2E/RT_s) \qquad (5a)$$

$$a = (KC_p/\pi e^2 \rho \, q^2 L^2 Z^2) \qquad (5b)$$

An estimate of T_s is required to use this equation.

Equations (2) and (4) give the energy required to ignite
an explosive as a function of the heating time for high heat
flux conditions. It was also mentioned, however, that some
minimum energy is always required to initiate an explosive,
below which energy ignition will not occur. This minimum
energy may be estimated from a slight modification of concepts
used in estimating the minimum ignition energy of gases, and
will be discussed in a subsequent paper.

The quantitative approach employed in this paper is that
ignition is a pure thermal reaction. However, it is known that
certain subsidiary factors such as chemical effects from certain
gases, such as oxygen, or catalytic effects from the heating
source may influence the ignition process. The inclusion of

these factors is beyond the scope of this paper, but it may be mentioned that their general influence should decrease as the temperature of the source and its accompanying heat flux is increased.

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References

(1) J. D. Morgan, Phil. Mag. 49, 323(1925).

(2) E. Jones, Proc. Roy. Soc. A198, 523(1949).

(3) G. T. Bryan and E. C. Noonan, Proc. Roy. Soc. 246, 167(1958).

(4) (a) Frank-Kamenetskii, Diffusion and Heat Exchange in Chemical Kinetics, Princeton University Press, Princeton, 1955, Chapt. VI; (b) B. L. Hicks, J. Chem. Phys. 22, 414(1954); (c) J. Zinn and R. N. Rogers, J. Phys. Chem. 66, 2646(1962)

(5) H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, Oxford University Press, London, 1947.

(6) M. A. Cook and M. T. Abegg, Ind. Eng. Chem. 48,1090(1956).

(7) (a) A. J. B. Robertson, Trans. Far. Soc. 44, 977(1948); (b) E. K. Rideal and A. J. B. Robertson, Proc. Roy. Soc. A195, 135(1948); (c) A. J. B. Robertson, Trans. Far. Soc. 45, 85(1949); (d) ibid., J. Soc. Chem. Ind. 51, 221(1948).

(8) C. H. Yang, Combn. & Flame, 6, 215(1962).

(9) H. F. Stout and E. Jones, Third Symposium (International) on Combustion, Williams and Wilkins Press, Baltimore, 1949, p. 329.